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Annotatio

Comment on the Kinetic Energy Components of LCAO-Molecular Orbitals by Harold Baumann and Edgar Heilbronner

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In a recent article by BAUMANN and HEILBRONNER [1], the analogy between the wave functions for the "electron-in-a-box" model and the LCAO–MO counterparts for an electron in a π system was discussed. One of the integrals needed for this work was the quantity A, Eq. (42) of their text

$$A = \tfrac{1}{4} R^2 \int_1^\infty e^{-R\mu} \log \frac{(\mu+1)}{(\mu-1)} [1 - R\mu - 6\,\mu^2 + 2\,R\mu^3 + 5\,\mu^4 - R\mu^5]\, d\mu \qquad (1)$$

which was integrated numerically.

In tables of molecular integrals, KOTANI et al. [2] define

$$f_0(m, \alpha) = \int_1^\infty \tfrac{1}{2} ln \left(\frac{\mu+1}{\mu-1}\right) e^{-\alpha\mu}\, \mu^m\, d\mu \qquad (2)$$

and analytically obtain for the two lowest members of the series

$$f_0(0, \alpha) = (2\,\alpha)^{-1} \{(C + \log 2\,\alpha)\, e^{-\alpha} + [-E_i(-2\,\alpha)]\, e^{\alpha}\} \qquad (3a)$$

and

$$f_0(1, \alpha) = (2\,\alpha^2)^{-1} \{(C + \log 2\,\alpha)\,(1 + \alpha)\, e^{-\alpha} + [-E_i(-2\,\alpha)]\,(1 - \alpha)\, e^{\alpha}\} \qquad (3b)$$

where $C = 0.577215\ldots$ is Euler's constant and $[-E_i(-2\,\alpha)]$ is the standard notation for the exponential integral.

Using (3a), (3b) and the recurrence relation for the $f_0(m, \alpha)$

$$f_0(m, \alpha) = f_0(m - 2, \alpha) + \alpha^{-1} \{m f_0(m - 1, \alpha) - (m - 2)\, f_0(m - 3, \alpha) - A_{m-2}(\alpha)\} \qquad (4)$$

where

$$A_n(\alpha) = \int_1^\infty x^n\, e^{-\alpha x}\, dx\,, \qquad (5)$$

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we obtain the following simple expression for the integral A of (1):

$$A = 3\, R^{-2}\, e^{-R}\, (1 + R + R^2/3)\,. \tag{6}$$

Substituting this expression for A into (32) and (33) of BAUMANN and HEILBRONNER, we find* for the kinetic energy T_J associated with the orbital ψ_J and the corresponding components T_{J_x}, T_{J_y}, T_{J_z}

$$T_{J_x} = \tfrac{1}{6}\,\zeta^2[1 + \chi_J\, e^{-R}(1 + R - R^2)]/(1 + \chi_J\, S) \tag{7a}$$

$$T_{J_y} = T_{J_z} = \tfrac{1}{6}\,\zeta^2[1 + \chi_J\, e^{-R}(1 + R)]/(1 + \chi_J\, S) \tag{7b}$$

$$T_J = \tfrac{1}{2}\,\zeta^2[1 + \chi_J\, e^{-R}(1 + R - R^2/3)]/(1 + \chi_J\, S)\,. \tag{7c}$$

The kinetic energy corrections $T_{\mu\nu,x}$, $T_{\mu\nu,y}$, and $T_{\mu\nu,z}$ associated with the overlap regions $\phi_\mu\, \phi_\nu$ of bonded centers has the following simple forms

$$T_{\mu\nu,x} = \tfrac{1}{6}\,\zeta^2(1 + R - R^2)\, e^{-R}\,, \tag{8a}$$

$$T_{\mu\nu,y} = T_{\mu\nu,z} = \tfrac{1}{6}\,\zeta^2(1 + R)\, e^{-R}\,. \tag{8b}$$

Using the analytical forms above in (7) and (8), a recalculation of their Tab. 1 and 2 was made and no major corrections were found as compared to their numerical methods of integration.

* See [1] for notation and definition of all terms.

References

1. BAUMANN, H., and E. HEILBRONNER: Theor. chim. Acta **6**, 95 (1966).
2. KOTANI, M., A. AMEMIYA, E. ISHIGURO, and T. KIMURA: Tables of molecular integrals, p. 58—59. 2nd Edition. Tokyo: Maruzen Co., Ltd. 1963.

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